Solar cells using bulk crystals of rare metal − free compound semiconductor $ZnSnP_2$

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Abstract

We report on the performance of solar cells using $ZnSnP_2$ compound semiconductor consisting of safe and earth-abundant elements for the first time. The minority carrier lifetimes in bulk crystals of $ZnSnP_2$ were 0.44 and 14 ns, which were obtained by analysis using double exponential function in time-resolved photoluminescence. The lifetime is close to that of CIGS, which is as high as to achieve the conversion efficiency of over 16%. The structure of an Al/Al-doped ZnO/ZnO/CdS/$ZnSnP_2$/Mo was adopted for the fabrication of solar cells. The short-circuit current density and the open circuit voltage are 2 mA/cm^2 and 0.17 V, respectively. The wavelength at the absorption edge in external quantum efficiency is consistent with the bandgap of $ZnSnP_2$. However, the conversion efficiency is approximately 0.09 %, and higher performance is required. The current density−voltage curve suggests that the reduction of series resistance is needed because it is higher than the value expected from the resistivity of bulk $ZnSnP_2$. The improvement of conduction band offset is also necessary considering from our previous works.

1 Introduction

Solar cells using compound semiconductors have made huge progress in recent years. In particular, the solar cells based on $CuIn_{1-x}Ga_xSe_2$ (CIGS) and CdTe have achieved high conversion efficiencies of 22.3 [1] and 22.1 %,[2] respectively. However, the use of rare or toxic elements suppresses the widespread use of these materials. From these backgrounds, solar absorbing materials composed of earth-abundant and safe elements have been investigated and $Cu_2ZnSnS_{4-x}Se_x$ solar cells have been developed with a conversion efficiency of 12.6%.[3] The other compounds, such as Cu_2SnS_3,[4] Cu_2O,[5] SnS,[6] Fe_2S [7] and Zn_3P_2 [8] have been also researched for the same purpose.

$ZnSnP_2$ has been proposed as a promising candidate for a solar absorbing material consisting of earth-abundant and safe elements. In the previous works, it was reported that $ZnSnP_2$ with a chalcopyrite structure showed a p-type conduction with the carrier concentration in a range of 10^{16}–10^{18} cm^{-3} [9-16] and has a direct bandgap of 1.6 – 1.7 eV.[14-17] According to Shockley–Queisser theory,[18] the conversion efficiency of over 30 % is calculated in single-junction cells with $ZnSnP_2$ absorber under an AM 1.5G solar

spectrum.[19] In addition, the absorption coefficient of $ZnSnP_2$ is about 10^5 cm^{-1} in the visible light region[19,20], which is close to that of CIGS. [19, 21]

As mentioned above, $ZnSnP_2$ is suitable as an absorber material from the viewpoints of electrical and optical properties, however, solar cells based on $ZnSnP_2$ have not been reported yet. In our group, the bulk crystals of $ZnSnP_2$ with the diameter of ~ 8 mm were prepared by solution growth with the slow cooling rate of ~ 0.7 °C/h.[16] The obtained crystals demonstrated the p-type characteristic with the hole density of 10^{16}–10^{18} cm^{-3}, which was measured by van der Pauw method.[16] The size of our crystals is larger than the reported $ZnSnP_2$ crystals with the dimension of ~ 4 × 4 mm^2 and the thickness of ~0.5 mm, which were obtained by the rapid cooling rate of 10~50 °C/h.[10, 11, 13, 14] Accordingly, our crystals with relatively large diameter was utilized for the fabrication of solar cells. We here report on photovoltaic performance of solar cells using $ZnSnP_2$ bulk crystals as a solar absorber for the first time.

2 Experimental methods

$ZnSnP_2$ bulk crystals were prepared by flux method, a kind of solution growth, reported in our previous work.[16] For the crystal growth, raw materials, Zn shots (99.99 %, Kojundo Chemical Laboratory), Sn shots (99.99 %, Kojundo Chemical Laboratory) and red phosphorus flacks (99.9999 %, Kojundo Chemical Laboratory) were sealed in an evacuated quartz ampoule below 10^{-2} Pa. Then, the quartz ampoule was set in the vertical furnace and heated up to 700 °C for homogenization. The crystal growth was performed from the bottom by moving up the furnace. The moving rate was controlled as the cooling rate of the quartz ampoule was approximately 0.7 °C/h. The temperature of the bottom of the ampoule was monitored by a thermocouple during the $ZnSnP_2$ crystal growth. The grown $ZnSnP_2$ bulk crystals were cut into wafers with the diameter of ~ 8 mm and the thickness of 0.5 mm. The surface of the wafer was mechanically polished with emery papers and finally 1 mm diamond slurry on a buff sheet.

The obtained crystals were evaluated by photoluminescence (PL) and time-resolved photoluminescence (TRPL) at room temperature using the measurement system of

luminescence lifetime (Hamamatsu Photonics, C12132). The wavelength and the power of the excitation laser were 532 nm and 1.87 mW, respectively, and the beam area was 1.02 mm^2. We adopted the structure of Al/Al-doped ZnO(AZO)/ZnO/CdS/$ZnSnP_2$/Mo for the fabrication of solar cells, which is similar to that of CIGS solar cells.[22] First of all, Mo back electrode was deposited with the thickness of approximately 800 nm by direct current (DC) sputtering on the polished surface of $ZnSnP_2$ wafers. Then, CdS buffer layer with the thickness of approximately 50 nm, which is widely used as buffer layer of CIGS based solar cells with a conversion efficiency of above 20 %,[22] was prepared on the opposite surface to Mo electrode by chemical bath deposition (CBD) method, where the solution composed of $CdSO_4$ (1.1 mmol/L), ammonia (2.3 mmol/L) and thiourea (56 mmol/L) was used. The temperature and the deposition time were 80 °C and 11 min, respectively. Subsequently, ZnO and AZO films were formed by radio frequency (RF) magnetron sputtering at room temperature with the thicknesses of 50 and 300 nm, respectively. For the fabrication of ZnO and AZO films, ZnO (99.99 %, Furuuchi Chemical) and ZnO-2 wt.% Al_2O_3 (99.99 %, Furuuchi Chemical) were used as target

materials. Finally, Al electrode with a grid pattern was fabricated by electron-beam evaporation. The current density−voltage (*J*−*V*) characteristics and the external quantum efficiency (EQE) of the solar cells were investigated under the illumination conditions of 100 mW/cm^2 and AM 1.5 G using the measurement system with solar simulator (Bunkoukeiki, CEP-25RR).

3 Results and discussion

Figure 1 shows the PL spectrum of a $ZnSnP_2$ bulk crystal evaluated at room temperature, which indicates that the PL peak position is observed at the photon energy of approximately 1.67 eV. This value is well consistent with the bandgap of $ZnSnP_2$ with a chalcopyrite structure as reported in the previous works.[14-17] Therefore, it is considered that the peak of PL spectrum shows a band to band transition in the $ZnSnP_2$ bulk crystals. However, the spectrum is broad especially in lower photon energy region. This might be attributed to damage layer at the surface of crystals or defects such as antisite atoms, which make narrower bandgap due to low degree of order.[23] Subsequently, TRPL

measurements were performed at the photon energy of 1.67 eV. TRPL lifetimes were thus evaluated by the following function as shown in Fig. 2,

$$I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2), \quad (1)$$

where t is the time after the laser excitation, $I(t)$ is the luminescence intensity at t, τ_1 and τ_2 are the fast and slow components of TRPL lifetimes, A_1 and A_2 are the pre-exponential factors, respectively. The fast and slow components of TRPL lifetimes, τ_1 and τ_2, were evaluated to be ~ 0.44 and ~ 14 ns, respectively, from the gradient of the lines in the figure. Chantana *et al.* reported that the lifetimes of CIGS thin films, which leads to the conversion efficiency of 16.22 %, were ~ 1 and ~ 10 ns for τ_1 and τ_2 , respectively.[24] The measurements for the CIGS films and $ZnSnP_2$ crystals were carried out using the same instrument. It is thus understood that the lifetime of $ZnSnP_2$ is close to that of CIGS. In late years, candidates for solar absorbing materials have been investigated using the TRPL measurement and the importance of a high TRPL lifetime is discussed.[25-28] Hence, it is considered that $ZnSnP_2$ is one of promising candidates from the viewpoint of carrier lifetime.

Solar cell with a structure of an Al/AZO/ZnO/CdS/$ZnSnP_2$/Mo was fabricated and its performance was investigated. Figures 3 and 4 exhibit the *J*−*V* characteristics and the EQE spectrum of the corresponding solar cell. The cell parameters are also shown in Fig. 3. We can significantly observe the photocurrent, and the wavelength of the absorption edge is evaluated to be approximately 1.64 eV, which is basically consistent with the PL spectrum shown in Fig.1 and the reported bandgap of $ZnSnP_2$.[14-17] We here give the first report on the solar cells with a certain absorber of $ZnSnP_2$.

However, the cell performance is still low for a practical use; the conversion efficiency is ~ 0.09 %. The mature device structure is usually adopted for solar cells using novel absorbers at the first step, and then its problems should be investigated and improved to achieve higher efficiency.[29, 30] In $ZnSnP_2$ solar cells, the series resistance was roughly evaluated to be 100 Ωcm^2 from the forward bias *J*−*V* characteristics, which might lead to the small value of the short circuit current density, J_{SC}. The resistivity of $ZnSnP_2$ bulk crystals measured by van der Pauw method is 10-70 Ω cm [16] and the resistance can be thus calculated to be less than 3.5 Ωcm^2 for $ZnSnP_2$ wafers with the thickness of 0.5 mm.

Hence, the large series resistance comes from resistances at the interfaces of CdS/$ZnSnP_2$ and/or $ZnSnP_2$/Mo, and the further investigation is necessary to clarify the effect of interfaces. On the other hand, the small value of the open circuit voltage, V_{OC}, 0.175 V, might be attributed to the large conduction band offset (CBO) between CdS and $ZnSnP_2$, −1.2 eV,[31] which makes a cliff at their interface and limits the value of V_{OC}. In the view point of the conduction band offset, it was suggested that ZnS and In_2S_3 were suitable materials as a buffer layer. From the spectrum shown in Fig.4, EQE is reduced at round 650 nm. One of the reasons is considered to be the bulk recombination of carries generated in deep region of $ZnSnP_2$ crystals due to narrow depletion layer, but it is unclear. Therefore, this point should be investigated and improved for higher conversion efficiency of $ZnSnP_2$ solar cells.

4 Conclusion

We demonstrated the performance of solar cells using $ZnSnP_2$ compound semiconductor as an absorber. The PL measurements were carried out and the carrier lifetimes in bulk crystals of $ZnSnP_2$ were 0.44 and 14 ns, which were obtained by analysis using double exponential function in time-resolved photoluminescence. The lifetime of $ZnSnP_2$ is close to that of CIGS, which leads to high conversion efficiency of over 16 %.

The solar cell with the structure of an Al/AZO/ZnO/CdS/$ZnSnP_2$/Mo was prepared. It is really understood that $ZnSnP_2$ is an absorber in the solar cell in this work from the measurements of *J*−*V* characteristics and EQE. However, the performance of the solar cells is quite low and some problems should be improved to achieve higher conversion efficiency. First, the higher series resistance, approximately 100 Ωcm^2, should be reduced. The resistance of the absorber $ZnSnP_2$ was calculated to be 3.5 Ω cm^2 from the resistivity. Therefore, it is necessary to improve the resistance at the heterointerfaces. On the other hand, low open circuit voltage might be attributed to large CBO at CdS/$ZnSnP_2$ interface and appropriate buffer materials should be developed. In addition, relatively low EQE at

around 650 nm should be improved for higher current density. As described above, we can understand that $ZnSnP_2$ has a great potential for solar cells with higher efficiency although the present efficiency is low. This work is really a start point for the development of $ZnSnP_2$ solar cells.

Acknowledgements

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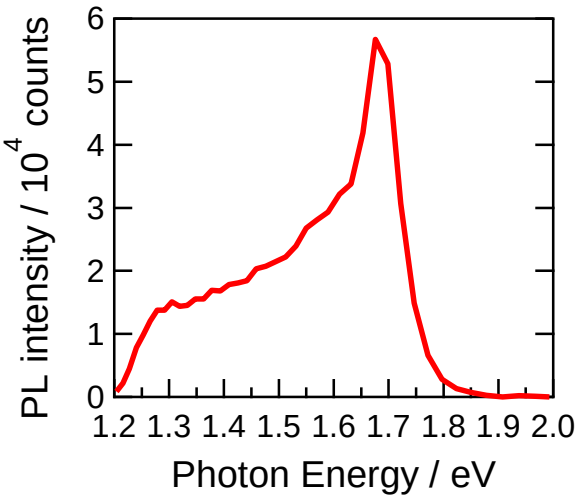
Figure captions

Figure 1 PL spectrum of $ZnSnP_2$ bulk crystal at room temperature. For the measurement, an excitation laser with the wavelength of 532 nm was used. The laser power and the beam area were set at 1.87 mW and 1.02 mm^2, respectively.

Figure 2 TRPL decay curve of $ZnSnP_2$ bulk crystal at room temperature. The decay curve was measured at the photon energy of 1.67 eV. The lifetime was evaluated by the double exponential function: $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$.

Figure 3 $J-V$ characteristics of the solar cell with the structure of an Al/AZO/ZnO/CdS/$ZnSnP_2$/Mo. The characteristics were measured with and without the illumination of AM 1.5 G.

Figure 4 EQE spectrum of the solar cell with the structure of an Al/AZO/ZnO/CdS/$ZnSnP_2$/Mo.



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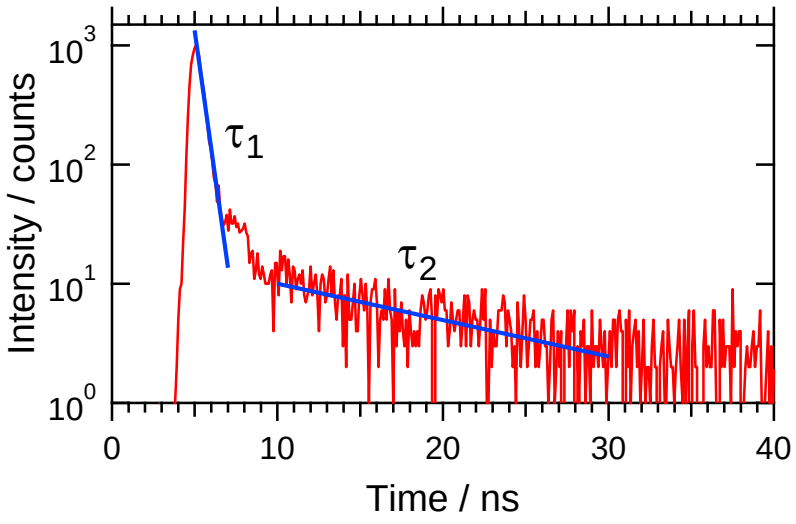

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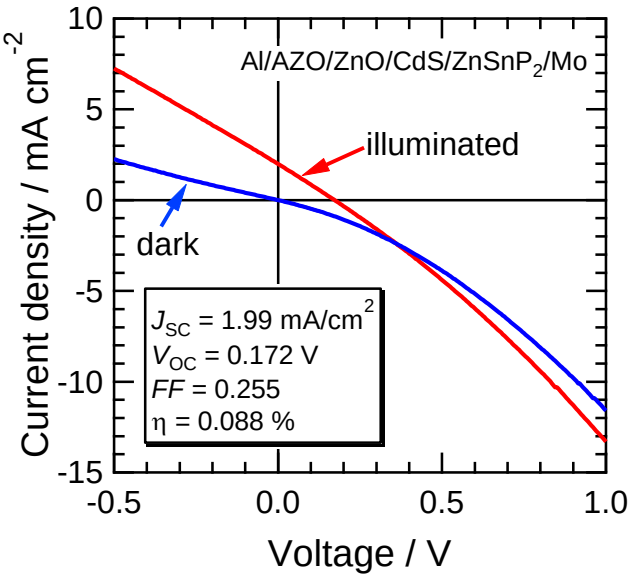

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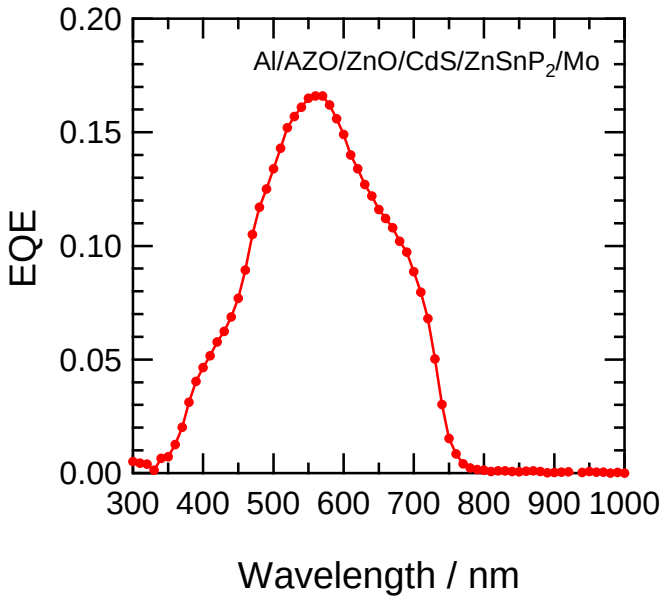

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